Journal of Catalysis **182,** 264–269 (1999)
Article ID jcat.1998.2336, available online at http://www.idealibrary.com on IDEAL®

RESEARCH NOTE

# Transient Kinetic Analysis of the Oxidative Dehydrogenation of Propane

D. Creaser,‡ B. Andersson,† R. R. Hudgins,*[,1] and P. L. Silveston*

*Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada; †Department of Chemical Reaction Engineering, Chalmers University of Technology, S-412 96, Göteborg, Sweden; and ‡Chemical Technology, Luleå University of Technology, S-971 87 Luleå, Sweden

Received May 11, 1998; revised November 18, 1998; accepted November 19, 1998

**Oxidative dehydrogenation of propane was studied using various transient techniques. Results support a redox mechanism in which propane reduces the catalyst, which is reoxidized by gas-phase oxygen. Only lattice oxygen participates in propene formation. Desorbable oxygen is a major source of poor selectivity, although lattice oxygen also causes total oxidation. Consequently, propene selectivity in the absence of gas-phase $O_2$ is superior to co-feed, steady-state selectivity at the same propane conversion. Propene selectivity is further improved by increasing the degree of catalyst reduction.** © 1999 Academic Press

*Key Words:* **propane oxidative dehydrogenation; V–Mg–O; transient analysis.**

Poor selectivity in the oxidative dehydrogenation of alkanes has been a problem preventing commercial exploitation of this process. A better understanding of the mechanism of oxidative dehydrogenation would permit identification of factors limiting the selectivity. Most researchers favor a Mars–Van Krevelen redox mechanism involving reduction of the metal oxide surface by alkane with the formation of alkene and water, followed by reoxidation of the surface through gas-phase oxygen. Zanthoff *et al.* (1) summarize mechanisms and surface properties proposed in the recent literature for selective oxidative dehydrogenation. In an earlier steady-state study (2), the authors observed that several Mars–Van Krevelen redox models would fit the measurements but were unable to decide which model was most appropriate. Our inability to resolve the models is not surprising, since it is difficult to deduce mechanism from kinetic data collected at steady state. Transient data are more effective. The use of transient response for investigation of mechanism has been reviewed by Kobayashi and Kobayashi (3), among others. These methods have been applied to to oxidative dehydrogenation. Sloczynski (4) examined reduction and reoxidation reactions from cyclic experiments for the oxidative dehydrogenation of $C_3H_8$ over $V_2O_5/TiO_2$, while Pantazidis and Mirodatos (5) used transient and isotope exchange experiments to propose a qualitative mechanism for the reaction over Mg–V–O catalyst.

In this contribution, various transient techniques such as startup, reaction interruption, and pulsing are used to identify steps in the reaction mechanism, estimate amounts of intermediates or reaction by-products adsorbed, and determine the degree of reduction of the catalyst surface. A practical goal of our study was to evaluate whether an unsteady-state operation could minimize complete oxidation of $C_3H_8$.

The same batch of catalyst used in our earlier study of the steady-state kinetics of oxidative dehydrogenation (2) was used for this investigation. It contained 60 wt% MgO and 40 wt% $V_2O_5$. X-ray diffraction indicated that the principal phases were magnesium oxide and magnesium *ortho*-vanadate [$Mg_3(VO_4)_2$].

Experiments were performed in a quartz microreactor containing 15 to 40 mg of catalyst. Details of reactor design have been published (3). All experiments were conducted isothermally at 510°C. Total flow rate was 50 ml (STP)/min; pressure was close to atmospheric.

A quadrupole mass spectrometer with a computerized data acquisition system was used to monitor the transient response of each component and allowance was made for cross-contributions among component peaks. Details of the mass spectrometry (MS) data analysis are given by (6). To verify the MS results, concentrations of carbon-containing products were measured in parallel by gas chromatography (GC) at a much lower frequency. GC analysis established that the only carbon-containing products were $C_3H_6$, $CO_2$, and CO. Creaser and Andersson (2) described the GC analysis.

Figure 1 shows results of a step-change from an initial feed containing 6% $O_2$ to a reaction mixture of 6% $O_2$ and 3% $C_3H_8$ employing 21 mg of fresh catalyst. The step-change occurs at time zero. From the delay in the appearance of $C_3H_8$ in the off-gas, the transport lag due to gas holdup for the reactor system was about 9 s. Buildup of

---

[1] To whom correspondence should be addressed.

0021-9517/99 $30.00

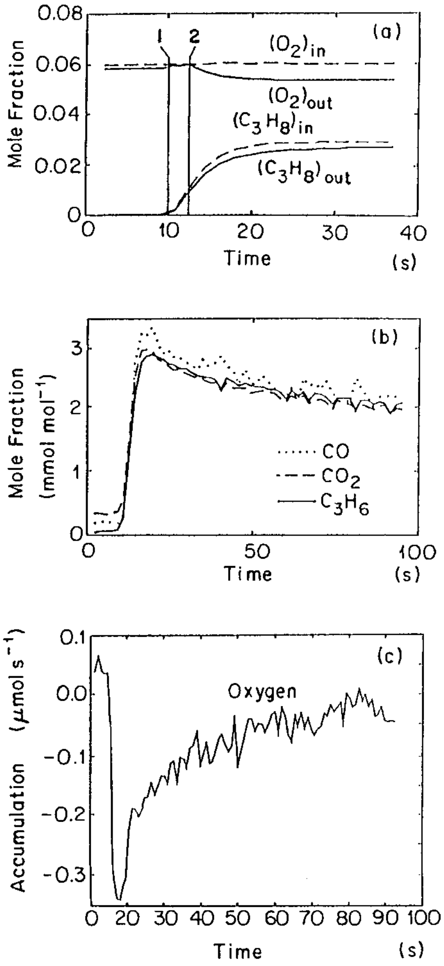

**FIG. 1.** (a) Reactant responses, (b) product responses on startup, and (c) rate of consumption of $O_2$ in the catalyst with a feed containing 6% $O_2$ and 3% $C_3H_8$ with 21 mg catalyst. Broken curves in (a) show responses when catalyst is replaced by inert solid of identical size and shape.

$C_3H_8$ indicates distortion of the square-wave input due to mixing. Broken curves in Fig. 1a show inlet concentrations of the reactants estimated by performing the step-change with catalyst replaced by quartz chips of identical size and shape. Figure 1a shows that with the fully oxidized fresh catalyst, $C_3H_8$ consumption begins (vertical line 1) about 4 s sooner than $O_2$ consumption (vertical line 2). Gas-phase $O_2$ is consumed only after the catalyst is partially reduced.

Initially, with a fully oxidized catalyst, the reaction rate is high, resulting in a peak in product concentrations (Fig. 1b). As the catalyst is reduced, reaction rates of the three products fall together. It takes about 2000 s to reach steady state, so Fig. 1b indicates only that the initial responses of the three carbon-containing products are nearly identical.

Figure 1c shows the instantaneous rate of consumption of $O_2$ on or in the catalyst as obtained by mass balances. Water has been excluded from these balance calculations because the water response is distorted by adsorption in the mass spectrometer chamber. Instead, the quantity of water leaving the reactor is assumed to correspond stoichiometrically to the quantity of the other products detected. The response in Fig. 1c exhibits noise because is it calculated from differences between much larger concentrations. Nevertheless, rapid depletion of $O_2$ occurring on startup exceeds significantly the average amplitude of the noise and trends are certainly discernible. For example, after about 150 s, there is virtually zero $O_2$ depletion. Integrating with respect to time between 10 and 150 s gave 15 $\mu$mol as the total quantity of $O_2$ removed from the magnesium *ortho*-vanadate phase. Thus, in the approach to steady state, 4.1% of the maximum $O_2$ available is consumed. This means that just the near surface of the catalyst provides $O_2$ and participates in the redox chemistry.

Carbon accumulated on the surface but the amount was very small. Carbon accumulation began about 30 s later than the sharp depletion of $O_2$ in Fig. 1c, but terminated when $O_2$ ended.

Figure 2 shows product transients following interruption of the reaction by a switch to a new feed composition. In Fig. 2a, the step-change was made from the steady-state $C_3H_8/O_2$ feed to pure He, while in Fig. 2b, it was made from the steady-state feed to an oxygen/He mixture. The concentration of $C_3H_8$ and quantities of catalyst also differed. In Fig. 2a, the increase in $C_3H_6$ prior to 10 s is a transport lag effect. It is noticeable that the peak in $C_3H_8$

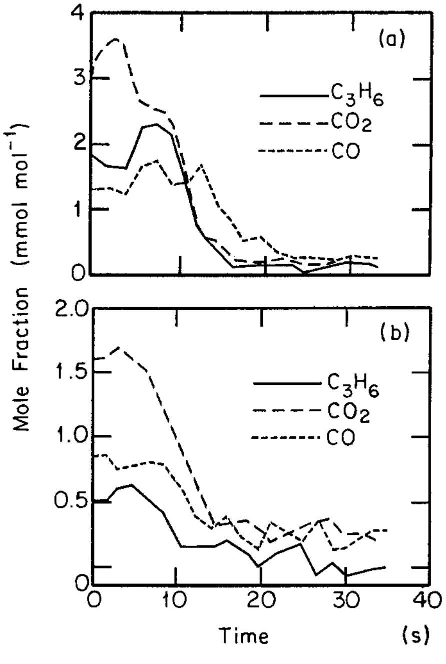

**FIG. 2.** Product transient responses (a) after interruption of catalyst exposure to 6% $C_3H_8$ and 6% $O_2$ by switching to pure He for 30 mg catalyst and (b) after interruption of exposure to 3% $C_3H_8$ and 6% $O_2$ for 21 mg catalyst by switching off $C_3H_8$.

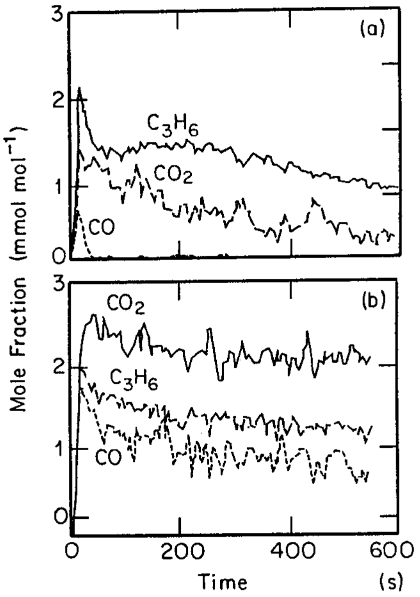

**FIG. 3.** Product responses to startup with a catalyst exposed initially to 6% $O_2$ using (a) 6% $C_3H_8$ and (b) 6% $C_3H_8$ and 6% oxygen.

corresponds to a drop in $CO_2$ as $O_2$ is removed from the system. Thus, once the reactants are removed, $C_3H_6$ and CO desorb but are not oxidized because $O_2$ is no longer available. For a step-change to pure He, the CO response lags those of $C_3H_6$ and carbon dioxide. The lag is about 5 s for $CO_2$ and CO. The lag in Fig. 2b is smaller because gas flows are higher. Concentrations of all carbon-containing products decrease following the change when the transport lag is allowed for.

The quantity of carbon on the catalyst surface prior to a step-change to He (Fig. 2a) was crudely estimated by integrating the area below the CO response curve and above the $CO_2$ and $C_3H_6$ response curves. It was found to be about 0.23 $\mu$mol (the catalyst contained 132 $\mu$mol of V).

For the step-change to $O_2$ and He, $O_2$ was adsorbed and the catalyst reoxidized. The quantity of $O_2$ accumulated on the catalyst following the switch was 6.7 $\mu$mol. When the reaction was started with fresh catalyst, about 15 $\mu$mol of $O_2$ was removed. Thus, less than half of the $O_2$ removed is replaced by reoxidation. The catalyst, for which the reaction was interrupted with a step-change to pure He, was also reoxidized later by exposure to 6% $O_2$ at the reaction temperature. Again, only a fraction of the original $O_2$ removed was eventually replaced.

These experiments were performed to determine how much $O_2$ the catalyst can provide to drive the reaction and to test reoxidation of the catalyst. Selectivity was also of interest. In these experiments, the catalyst was reduced by reaction with $C_3H_8$ and then reoxidized with $O_2$. Between the reduction and oxidation steps, the catalyst was sometimes flushed with pure He. Prior to all runs, the catalyst was maintained at steady state with a feed of 6% $O_2$ and 6% $C_3H_8$ for at least 3 h. In the four-part cycle experiments, the catalyst was first exposed to 6% $O_2$ for 10 min, followed by pure He for 5 min. Next, 6% $C_3H_8$ was fed for 10 min, again followed by 5 min of pure He. This process was repeated five times and the reaction temperature was maintained at 510°C throughout. Two-part cycle experiments were the same except that the He flush steps were omitted.

Figure 3a shows the product concentrations following exposure to $C_3H_8$ for a four-part cycle experiment with 17 mg of catalyst. There is a sharp rise in concentration of all three carbon-containing products in the first 20 s following the switch to $C_3H_8$. After the maxima, product concentrations decrease quickly for about 30 s and thereafter decreased more slowly, indicating that the catalyst's supply of near-surface lattice or surface oxygen has been depleted. Production of hydrogen was not observed.

For comparison purposes, Fig. 3b shows product concentrations when the same quantity of catalyst is exposed alternately to $O_2$ and a gas containing 6% $C_3H_8$ and 6% $O_2$. Catalysts for Figs. 4a and 4b are in much the same condition

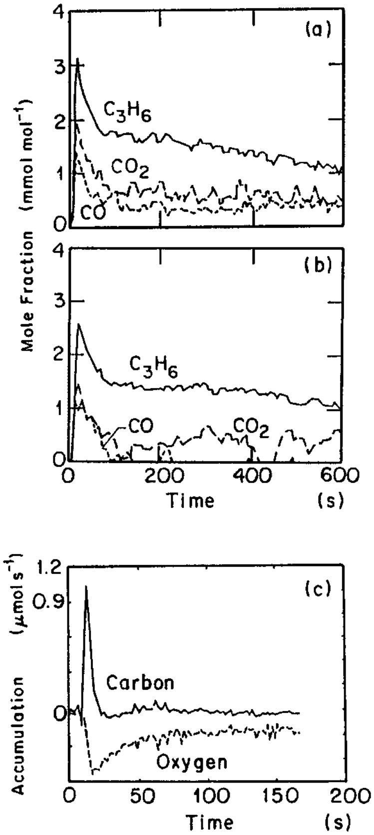

**FIG. 4.** Product responses for startup without gas-phase $O_2$ but with 6% $C_3H_8$ for a 30-mg catalyst sample using (a) a four-part cycle consisting of alternate exposures in the sequence $O_2$ : He : $C_3H_8$ : He, (b) a two-part cycle consisting of sequential exposures to $O_2$ and $C_3H_8$, and (c) rate of accumulation of carbon and depletion of oxygen on catalyst after startup with a four-part exposure cycle as in (a).

before the step-change to a $C_3H_8$-containing feed. The $C_3H_6$ concentrations in Figs. 4a and 4b are nearly identical immediately after the step-change and their variations with time are similar. However, the carbon oxide concentrations are considerably lower when $O_2$ is not present in the gas phase. In this case, selectivity to $C_3H_6$ is over 75%, while when $O_2$ is present it is about 60%. When a switch to a mixture of $C_3H_8$ and $O_2$ is used, Fig. 3b shows decays after the product maxima are slower. Furthermore, CO continues to be formed, whereas, on the switch to 6% $C_3H_8$ alone, it disappears from the products after about 50 s. These results indicate that adsorbed oxygen plays a role in the total oxidation steps that is different from that of the lattice oxygen, even though lattice oxygen does produce total oxidation. During cyclic experiments, the catalyst exhibited constant activity: each cycle of $C_3H_8$ exposure produced the same quantities of products.

Figure 4 compares product concentrations during alternate $O_2$ and $C_3H_8$ exposures, for two-part and four-part cyclic experiments with 30 mg of catalyst. In both cases, the $C_3H_6$ selectivity was more than 70%. Concentrations of all products were higher for the four-part cycle, but in view of Fig. 2, differences probably resulted from experimental variations. Product transients appear to be the same. Higher $C_3H_6$ selectivity with a four-part cycle was expected because of He flushing. In the two-part cycle some weakly bound, nonselective oxygen should remain on the catalyst surface after $O_2$ exposure. The amount must be very small because product responses in the two- and four-part cycles are so similar.

Figure 4c shows the accumulation rate of carbon during the first 180 s of exposure to $C_3H_8$ for the four-part cycle with 30 mg of catalyst. Carbon appears on the catalyst just after the 9-s transport lag and then accumulates rapidly during the next 20 s. The quantity of carbon that accumulates is about 5 μmol and does not vary from cycle to cycle. After 30 s, Fig. 4 suggests carbon accumulation ceases. In contrast, startup with gas-phase $O_2$ present and the reactant interruption experiments indicated very little carbon on the catalyst surface.

Figure 4c also shows the rate of oxygen removal from the catalyst. The time of the maximum depletion corresponds roughly to that for the maximum carbon deposition rate. Unlike carbon deposition, however, $O_2$ depletion continues for almost 90 s although at a decelerating rate. Integration indicated 74 μmol of $O_2$ was removed in the first cycle. This increased to about 97 μmol in the third cycle, after which it remained constant.

During $O_2$ partial cycles, the total quantity of $O_2$ adsorbed during the first 150 s varied between about 44 and 47 μmol, corresponding to about 8.5% of the removable $O_2$. Our measurements of the $O_2$ adsorbed account for only about half the $O_2$ removed by reaction with $C_3H_8$. Considering that the catalyst did not deactivate during successive cycles, the above discrepancy must arise from inaccuracies in mass balances, the $O_2$ depletion and recovery being calculated from differences between relatively large numbers. Immediately after a switch to $O_2$ during cycling, about 1.4 μmol of carbon oxides is produced. Again, this is much less than the carbon deposition during $C_3H_8$ exposure.

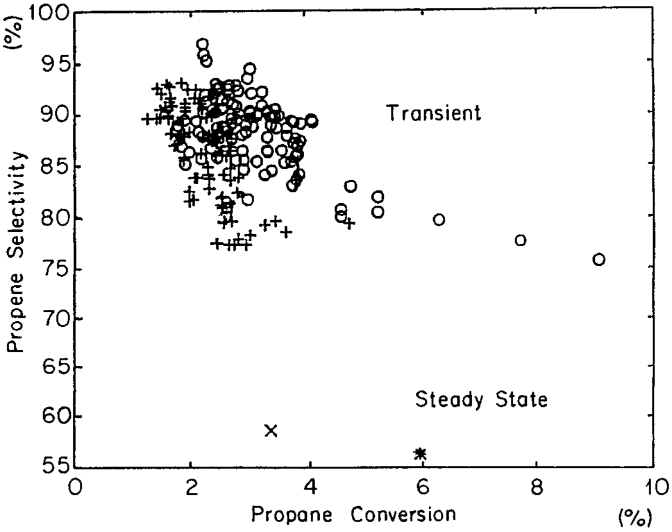

**FIG. 5.** Comparison of time-average $C_3H_8$ selectivity under step-change and steady-state operation at equal time-average $C_3H_8$ conversions. +, 17 mg catalyst, and ○, 30 mg catalyst, both with 10-min exposure to 6% $C_3H_8$; ×, 17 mg catalyst, and ∗, 30 mg catalyst, both with steady-state exposure to 6% $C_3H_8$ and 6% oxygen.

From a process standpoint, cycling experiments show that selectivity is increased by periodically switching between $C_3H_8$ and $O_2$. This is clearly seen in Fig. 5, which plots $C_3H_8$ selectivity against $C_3H_6$ conversion for two quantities of catalyst (17 and 30 mg) under the same reaction conditions under cycling and steady-state conditions. At the same conversion of $C_3H_8$, the figure shows much higher $C_3H_6$ selectivities are obtained in cyclic operation, i.e., in the absence of gas-phase oxygen. Propene selectivity increases as $C_3H_8$ conversion decreases. This behavior is anticipated because $C_3H_6$ is certainly an intermediate in $C_3H_8$ oxidation to $CO_2$ and water. The scatter in the figure at conversions between 2 and 4% results from inclusion of data for all cycles; we noted earlier that the catalyst is changing, certainly in the first cycles of an experiment.

Experiments were performed in which 20, 30, and 40 mg of catalyst were reduced by continuously switching between 6% $C_3H_8$ and He without any $O_2$ in the feed. The pulses were symmetrical, each lasting 30 s.

Under cycling between $O_2$ and $C_3H_8$, a maximum in product formation occurred after $C_3H_8$ was introduced and all products appeared simultaneously. Selectivity remained stable as the catalyst was depleted of oxygen. In $C_3H_8$ pulsing, the response was different. After the first pulse of $C_3H_8$, where there is a maximum in $C_3H_6$ production followed by a fast decline, a maximum is no longer observed and the activity returns to about the level in the previous pulse. Nevertheless, over 30 pulses, a decline in activity is observed.

In $C_3H_8$ pulsing, no lag in carbon oxide appearance was evident on switching to He, whereas a lag in the CO response was observed on switching to He in the reaction interruption experiments (Fig. 2a). The latter was thought to originate from the oxidation of carbon species on the catalyst. In $C_3H_8$ pulsing, there may not be sufficient $O_2$ remaining on the catalyst surface after the first $C_3H_8$ pulse to oxidize surface carbon species.

Figure 6 shows the average conversion, selectivity, and cumulative $O_2$ removal from the catalyst for each pulse of $C_3H_8$ in the $C_3H_8$ pulsing experiments. After the first pulse, there is a large decrease in $C_3H_8$ conversion, but in the next three to six pulses the conversion increases slightly before resuming its decrease. Propene selectivity increases as more $O_2$ is removed from the catalyst, while $C_3H_8$ conversion decreases. This is not the well-known inverse relation between conversion and selectivity to an intermediate product. Although conversion is higher with 30 mg of catalyst than with 20 mg, the selectivity differs little between these two masses of catalyst. Only with 40 mg of catalyst does conversion seem high enough to cause a drop in selectivity. Conversion drops to between 2.5 and 3% for the final pulses of $C_3H_8$ over 40 mg of catalyst, but this is about the conversion for the initial pulses over 20 mg of catalyst. The 40-mg catalyst sample, however, is considerably more reduced. Propene selectivity is about 86% for these pulses compared with between 75 and 80% for the initial pulses over 20 mg of catalyst. Part of the increase in $C_3H_6$ selectivity must be due then to a selectivity improvement as the catalyst is reduced. However, a large reduction of the catalyst is required before selectivity improves. Selectivity to $C_3H_6$ increases only after about 10 pulses and 15 to 20% $O_2$ removal. The literature suggests that this relation between selectivity and catalyst reduction results from increasing metal–oxygen bond strength for the reduced catalyst (7, 8). Our observations confirm experiments of Andersen and Kung (9) for the oxidative dehydrogenation of $C_4H_{10}$ over $V_2O_5/Al_2O_3$.

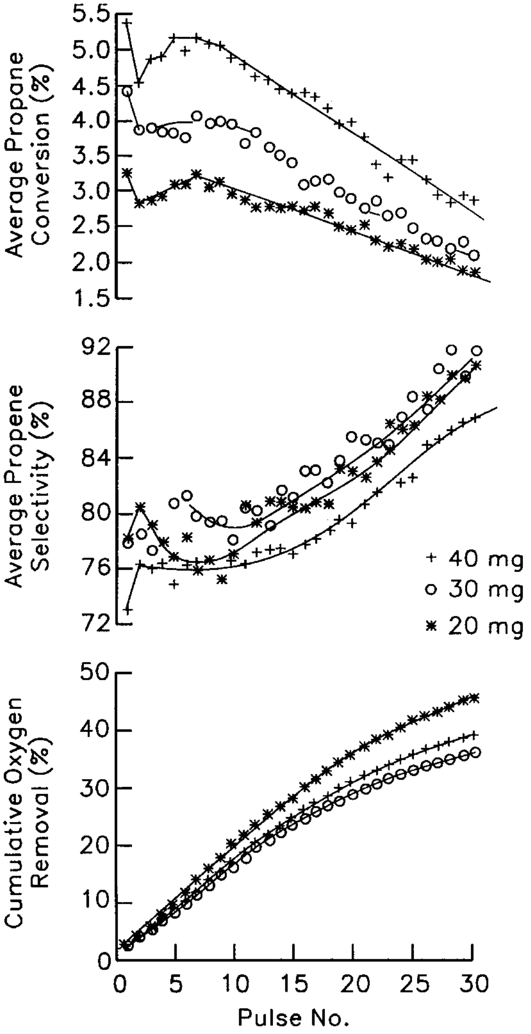

**FIG. 6.** Variation of time-average conversion, selectivity to $C_3H_6$, and cumulative $O_2$ removal from the catalyst for successive pulsing with $C_3H_8$.

The cumulative $O_2$ removal, shown in Fig. 6, is based only on the $O_2$ in the magnesium *ortho*-vanadate ($Mg_3V_2O_8$) phase. Reducing the vanadium from $V^{5+}$ to $V^{2+}$ corresponds to the removal of 37.5% of the $O_2$. After the 30 pulses of $C_3H_8$, vanadium would appear to be completely reduced to $V^{2+}$ in each catalyst sample. Perhaps some oxygen in the magnesium oxide is active and there may be additional adsorbed oxygen at or near the catalyst surface disregarded in bulk calculations. Regardless of the $O_2$ source, a relatively large quantity of $O_2$ is removed from the catalyst. Once again, hydrogen production was not observed, so oxidative dehydrogenation is the dominant reaction for production of $C_3H_6$ in these experiments, despite the reduction of the catalyst.

Temperature-programmed oxidation experiments were undertaken to verify the deposition of carbonaceous species during $C_3H_8$ pulsing experiments (11). A $CO_2$ peak is produced immediately after the switch to $O_2$ at about 530°C. A second peak occurs at about 640°C, indicating additional carbon species are on the catalyst that can be oxidized only at higher temperatures. These carbon species are also present on a catalyst operated under standard steady-state conditions. Only carbon species on the catalyst exposed to $C_3H_8$ pulsing seem to be oxidized at or near the reaction temperature of 510°C. Catalyst deactivation at steady-state conditions was not observed (3). Consequently, carbon species present on the catalyst and oxidized at elevated temperatures do not block active sites. Temperature-programmed desorption was also performed on catalyst samples from the $C_3H_8$ pulsing experiments Creaser *et al.* (10). Only small amounts of these oxides were observed, indicating that carbon oxides form from carbonaceous species on the catalyst surface rather than from adsorption.

For the oxidative dehydrogenation system considered in this paper, our experiments demonstrate that carrying out the reaction without gas-phase $O_2$ improves $C_3H_6$ selectivity even at the same conversion of $C_3H_8$. Thus higher selectivity and possibly yield could be achieved by operating the dehydrogenation reactor cyclically by switching between $C_3H_8$ and $O_2$ streams. Experiments were undertaken to test this proposition (11). These demonstrated a large improvement in selectivity, but a significant reduction in $C_3H_8$ conversion. For cycle periods exceeding 1 min, selectivities to $C_3H_8$ between 70 and 80% are observed, compared with just over 50% in steady-state operation. This improvement is sufficient to increase the yield of $C_3H_6$ by 35% at a cycle period of about 1 min. Our cyclic measurements thus support periodic operation as an option in a commercial oxidative dehydrogenation process.

Transient experiments support a redox reaction mechanism involving magnesium *ortho*-vanadate. Our observations indicate only lattice $O_2$ participates in $C_3H_6$ formation. Significant $O_2$ depletion occurs at startup to the steady state. Some carbon deposition also occurs, but this does not appear to block active sites. Larger amounts occur in switching between $O_2$ and $C_3H_8$, but most of this carbon is easily oxidized and does not contribute to deactivation. Our observations also predict the experimentally observed improvement in selectivity to the $C_3H_6$ product for a periodically operated reactor. In the absence of gas-phase $O_2$ following a step-change or startup, $C_3H_6$ selectivity was superior to that achieved at steady state, even at the same level of $C_3H_8$ conversion. A further increase in selectivity occurs when the catalyst is deeply reduced, beyond removal of about 20% of $O_2$ in the magnesium *ortho*-vanadate-phase. In the presence of gas-phase $O_2$, some active and deep oxidizing $O_2$ species form on the catalyst surface, leading to total combustion of adsorbed hydrocarbons.

## ACKNOWLEDGMENTS

This research would not have been possible without the financial support of The Swedish Board for Industrial and Technical Development and The Natural Sciences and Engineering Research Council of Canada.

## REFERENCES

1. Zanthoff, Pantazidis, A., and Mirodatos, C., *Chem. Eng. Sci.* (1998).
2. Creaser, D., and Andersson, B., *Appl. Catal. A* **141**, 131 (1996).
3. Kobayashi, H., and Kobayashi, M., *Catal. Rev. Sci. Eng.* **10**, 139 (1974).
4. Sloczynski, J., *Appl. Catal. A* **146**, 401 (1996).
5. Pantazidis, A., and Mirodatos, C., *in* "Proceedings, 11th International Congress on Catalysis" (J. W. Hightower, W. N. Delgass, E. Iglesia, and A. T. Bell, Eds.), Stud. Surf. Sci. Catal., Vol. 101, p. 1029 (1996).
6. Creaser, D., Ph.D. thesis, p. 28, University of Waterloo, Waterloo, Ontario, Canada, 1997.
7. Owen, O. S., Kung, M. C., and Kung, H. H., *Catal. Lett.* **12**, 45 (1992).
8. Patel, D., Andersen, P. J., and Kung, H. H., *J. Catal.* **125**, 132 (1990).
9. Andersen, P. J., and Kung, H. H., *in* "New Frontiers in Catalysis" (L. Guczi, F. Solymosi, and P. Teteryi, Eds.), Stud. Surf. Sci. Catal., Vol. 75, p. 205 (1993).
10. Creaser, D., Andersson, B., Hudgins, R. R., and Silveston, P. L., *Chem. Eng. Sci.*, in press (1999).
11. Creaser, D., Andersson, B., Hudgins, R. R., and Silveston, P. L., *Chem. Eng. Sci.*, in press (1999).